



# The Patent Office

The Patent Office  
Cardiff Road  
Newport  
Gwent  
NP9 1RH

the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation and Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the company of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Dated

12. 7. 1996

27 JUN 96 15:26:41 003022  
P01/7700 25.00

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

8757  
20 JUN 1996

2. Patent application number  
(The Patent Office will fill in this part)

9613227.9

25 JUN 1996

3. Full name, address and postcode of the or of each applicant (underline all surnames)

BP CHEMICALS LIMITED  
BRITANNIC HOUSE  
1 FINSBURY CIRCUS  
LONDON EC2M 7BA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

LA 41891002 +  
ENGLAND, UNITED KINGDOM

4. Title of the invention

ESTER SYNTHESIS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

KRISHNAN, Suryanarayana Kalyana  
BP INTERNATIONAL LIMITED  
GROUP PATENTS & AGREEMENTS  
CHERTSEY ROAD  
SUNBURY ON THAMES  
MIDDLESEX TW16 7LN

Patents ADP number (if you know it)

S683925001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country	Priority application number (if you know it)	Date of filing (day / month / year)
---------	-------------------------------------------------	----------------------------------------

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing (day / month / year)
-------------------------------	----------------------------------------

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

Continuation sheets of this form

Description 17

Claim(s)

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents  
(*please specify*)

11. I/We request the grant of a patent on the basis of this application.

Signature  Date 25.06.96  
KRISHNAN, Suryanarayana Kalyana

12. Name and daytime telephone number of person to contact in the United Kingdom 01932 762734

## Warning

*After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.*

## Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

### ESTER SYNTHESIS

The present invention relates to a process for the synthesis of esters by reacting an olefin with a lower carboxylic acid in the presence of an acidic catalyst.

5 It is well known olefins can be reacted with lower aliphatic carboxylic acids to form the corresponding esters. One such method is described in GB-A-1259390 in which an ethylenically unsaturated compound is contacted with a liquid medium comprising a carboxylic acid, a free heteropoly acid of molybdenum or tungsten. This process is a homogeneous process in which the heteropolyacid catalyst is unsupported. A further process for producing esters is  
10 described in JP-A-05294894 in which a lower fatty acid is esterified with a lower olefin to form a lower fatty acid ester. In this document, the esterification reaction is carried out in the gaseous phase in the presence of a catalyst consisting of at least one heteropolyacid salt of a metal eg Li, Cu, Mg or K, being supported on a carrier. The heteropolyacid used is phosphotungstic acid and the carrier  
15 described is silica.

It has now been found that the process efficiency can be improved significantly by co-feeding water to the reaction mixture.

Accordingly, the present invention is a process for the production of lower aliphatic esters said process comprising reacting a lower olefin with a saturated  
20 lower aliphatic mono-carboxylic acid in the vapour phase in the presence of a heteropolyacid catalyst characterised in that an amount of water in the range from 1-10 mole % based on the total of the olefin, aliphatic mono-carboxylic acid and water is added to the reaction mixture during the reaction.

A feature of the invention is the addition of water as a component of the  
25 reaction mixture. Surprisingly, it has been found that the presence of water in the

reaction mixture in an amount of 1-10 mole %, preferably from 1 to 7 mole %, etg 1 to 5 mole %, based on the total feed enhances the stability of the catalyst and thereby enhances the efficiency of the process. Furthermore, the presence of water also reduces the selectivity of the process to undesired by-products such as eg oligomers and other unknowns, excluding diethyl ether and ethanol.

It has further been found that dosing the reaction mixture with amounts of di-ether such as eg diethyl ether, as a co-feed also reduces the formation of undesirable by-products. The amount of a di-ether co-fed is suitably in the range from 1 to 6 mole %, preferably in the range from 1 to 3 mole % based on the total reaction mixture comprising the olefin, the aliphatic carboxylic acid, water and diethyl ether. The di-ether may correspond to the by product diether from the reaction generated from the reactant olefin. Where a mixture of olefins is used, eg a mixture of ethylene and propylene, the di-ether may in turn be an unsymmetrical ether. The di-ether co-feed may thus be the by-product of the reaction which is recycled to the reaction mixture.

The term "heteropolyacids" as used herein and throughout the specification is meant to include the free acids. The heteropolyacids used to prepare the esterification catalysts of the present invention therefore include the free acids and co-ordination type salts thereof in which the anion is a complex, high molecular weight entity. Typically, the anion comprises 2-18 oxygen-linked polyvalent metal atoms, which are called peripheral atoms. These peripheral atoms surround one or more central atoms in a symmetrical manner. The peripheral atoms are usually one or more of molybdenum, tungsten, vanadium, niobium, tantalum and other metals. The central atoms are usually silicon or phosphorus but can comprise any one of a large variety of atoms from Groups I-VIII in the Periodic Table of elements. These include, for instance, cupric ions; divalent beryllium, zinc, cobalt or nickel ions; trivalent boron, aluminium, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium or rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulphur, tellurium, manganese nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium, antimony ions; hexavalent tellurium ions; and heptavalent iodine ions. Such heteropolyacids are also known as "polyoxoanions", "polyoxometallates" or "metal oxide clusters". The structures of some of the well known anions are named after the original researchers in this field and are known eg as Keggin, Wells-Dawson and Anderson-Evans-Perloff structures.

Heteropolyacids usually have a high molecular weight eg in the range from 700-

8500 and include dimeric complexes. They have a relatively high solubility in polar solvents such as water or other oxygenated solvents, especially if they are free acids and in the case of several salts, and their solubility can be controlled by choosing the appropriate counterions. Specific examples of heteropolyacids that may be used as the catalysts in the present invention include:

5	12-tungstophosphoric acid	-	$H_3[PW_{12}O_{40}].xH_2O$
	12-molybdophosphoric acid	-	$H_3[PMo_{12}O_{40}].xH_2O$
	12-tungstosilicic acid	-	$H_4[SiW_{12}O_{40}].xH_2O$
	12-molybdosilicic acid	-	$H_4[SiMo_{12}O_{40}].xH_2O$
10	Potassium tungstophosphate	-	$K_6[P_2W_{18}O_{62}].xH_2O$
	Sodium molybdophosphate	-	$Na_3[PMo_{12}O_{40}].xH_2O$
	Ammonium molybdodiphosphate	-	$(NH_4)_6[P_2Mo_{18}O_{62}].xH_2O$
	Sodium tungstonickelate	-	$Na_4[NiW_6O_{24}H_6].xH_2O$
	Ammonium molybdodicobaltate	-	$(NH_4)[Co_2Mo_{10}O_{36}].xH_2O$
15	Cesium hydrogen tungstosilicate	-	$Cs_3H[SiW_{12}O_{40}].xH_2O$
	Potassium molybdodivanado phosphate	-	$K_5[PMoV_2O_{40}].xH_2O$

The heteropolyacid catalyst whether used as a free acid or as a salt thereof is suitably supported, preferably on a siliceous support. The siliceous support is suitably in the form of extrudates or pellets.

20 The siliceous support used is most preferably derived from an amorphous, non-porous synthetic silica especially fumed silica, such as those produced by flame hydrolysis of  $SiCl_4$ . Specific examples of such siliceous supports include Support 350 made by pelletisation of AEROSIL® 200 (both ex Degussa). This pelletisation procedure is suitably carried out by the process described in US Patent 5,086,031 (see especially the Examples) and is incorporated herein by reference. Such a process of  
 25 pelletisation or extrusion does not involve any steam treatment steps and the porosity of the support is derived from the interstices formed during the pelletisation or extrusion step of the non-porous silica. The silica support is suitably in the form of pellets or beads or are globular in shape having an average particle diameter of 2 to 10  
 30 mm, preferably 4 to 6 mm. The siliceous support suitably has a pore volume in the range from 0.3-1.2 ml/g, preferably from 0.6-1.0 ml/g. The support suitably has a crush strength of at least 2 Kg force, suitably at least 5 Kg force, preferably at least 6 Kg and more preferably at least 7 Kg. The crush strengths quoted are based on average of that determined for each set of 50 beads/globules on a CHATTILLON  
 35 tester which measures the minimum force necessary to crush a particle between parallel

plates. The bulk density of the support is suitably at least 380 g/l, preferably at least 440 g/l.

The support suitably has an average pore radius (prior to use) of 10 to 500 Angstroms, preferably an average pore radius of 30 to 100 Angstroms.

5 In order to achieve optimum performance, the siliceous support is suitably free of extraneous metals or elements which might adversely affect the catalytic activity of the system. The siliceous support suitably has at least 99% w/w purity, ie the impurities are less than 1% w/w, preferably less than 0.60% w/w and more preferably less than 0.30% w/w.

10 Another pelleted silica support is the Grace silica No. 1371 which has an average bulk density of about 0.39 g/ml, an average pore volume of about 1.15 ml/g and an average particle size ranging from about 0.1-3.5 mm. These pellets can be used as such or after crushing to an average particle size in the range from 0.5-2 mm and sieving before being used as the support for the heteropolyacid catalyst.

15 The impregnated support is suitably prepared by dissolving the heteropolyacid, which is preferably a tungstosilicic acid, in eg distilled water, and then adding the support to the aqueous solution so formed. The support is suitably left to soak in the acid solution for a duration of several hours, with periodic manual stirring, after which time it is suitably filtered using a Buchner funnel in order to remove any excess acid.

20 The wet catalyst thus formed is then suitably placed in an oven at elevated temperature for several hours to dry, after which time it is allowed to cool to ambient temperature in a desiccator. The weight of the catalyst on drying, the weight of the support used and the weight of the acid on support was obtained by deducting the latter from the former from which the catalyst loading in g/litre was determined.

25 Alternatively, the support may be impregnated with the catalyst using the incipient wetness technique with simultaneous drying on a rotary evaporator.

This supported catalyst (measured by weight) can then be used in the esterification process. The amount of heteropolyacid deposited/impregnated on the support for use in the esterification reaction is suitably in the range from 10 to 30 60% by weight, preferably from 30 to 50% by weight based on the total weight of the heteropolyacid and the support.

35 In the esterification reaction, the olefin reactant used is suitably ethylene, propylene or mixtures thereof. Where a mixture of olefins is used, the resultant product will inevitably a mixture of esters. The source of the olefin reactant used may be a refinery product or a chemical grade olefin which invariably contain

some alkanes admixed therewith.

The saturated, lower aliphatic mono-carboxylic acid reactant is suitably a C1-C4 carboxylic acid and is preferably acetic acid.

The reaction mixture suitably comprises a molar excess of the olefin reactant with respect to the aliphatic mono-carboxylic acid reactant. Thus the mole ratio of olefin to the lower carboxylic acid in the reaction mixture is suitably in the range from 1:1 to 15 : 1, preferably from 10-14:1.

The reaction is carried out in the vapour phase suitably above the dew point of the reactor contents comprising the reactant acid, any alcohol formed *in situ*, the product ester and water as stated above. The amount of water is in the range from 1-5 mole %, suitably from 1-5 mole % based on the total amount of olefin, carboxylic acid and water. Dew point is the temperature at which condensation of a vapour of a given sample in air takes place. The dew point of any vaporous sample will depend upon its composition. The supported heteropolyacid catalyst is suitably used as a fixed bed which may be in the form of a packed column. The vapours of the reactant olefins and acids are passed over the catalyst suitably at a GHSV in the range from 100 to 5000 per hour, preferably from 300 to 2000 per hour.

The esterification reaction is suitably carried out at a temperature in the range from 150-200°C using a reaction pressure which is at least 400KPa, preferably from 500-3000 Kpa depending upon the relative mole ratios of olefin to acid reactant and the amount of water used.

The reaction mixture may optionally contain steam if it is desired to generate a mixture of esters and alcohols in the process. The products of the reaction are recovered by eg fractional distillation. Where the esters are produced, whether singly or as mixture of esters, these may be hydrolysed to the corresponding alcohols or mixture of alcohols in relatively high yields and purity. By using this latter technique the efficiency of the process to produce alcohols from olefins is significantly improved over the conventional process of producing alcohols by hydration of olefins.

The present invention is further illustrated with reference to the following Examples and Comparative Tests.

#### Examples:

##### A. Catalyst Preparations:

##### Catalyst 1:



Silica granules (Grace 1371 grade,  $\text{m}^2/\text{g}$ , bulk density 0.39 g/ml, pore volume 1.15 ml/g, ca. 1-3 mm, 70 g, ex W R Grace) were soaked over 24 hours with intermittent stirring in a solution of silicotungstic acid [ $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$ ] (65.53 g, ex Japan New Metals) dissolved in 250 ml distilled water in order to impregnate the silica support with the silicophosphoric acid catalyst. After this duration, excess catalyst solution was decanted and filtered off. The resultant catalyst impregnated support was then dried in flowing nitrogen gas overnight at 120°C. The supported catalyst so formed was then left in a desiccator to cool and was finally reweighed. The resultant supported catalyst had a final weight of ..... g and a heteropolyacid catalyst loading of 92 g/litre.

Catalyst 2: Silica granules (Grace 57 grade, surface area 510  $\text{m}^2/\text{g}$ , bulk density 0.649 g/ml, pore volume 1.0267 ml/g, ca. 5-8 mm, 57.7 g, ex W R Grace) was soaked in a solution of 12-tungstosilicic acid [ $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$ ] (ex Johnson Matthey, 69.4 g dissolved in 200 ml distilled water) for 24 hours with intermittent stirring in order to impregnate the support with the catalyst. Thereafter the excess solution of the silico tungstic acid catalyst was removed by decantation and filtration. The resultant catalyst impregnated support was then dried overnight under flowing nitrogen at 120°C. The dried supported catalyst so formed was cooled in a desiccator and had a heteropolyacid catalyst loading of 190g/litre.

Catalyst 3: The above process of Catalyst 2 was repeated and was found to have a heteropolyacid catalyst loading of 192 g/litre.

#### B. Catalyst Forming:

All the catalysts produced above were broken down and sieved to obtain the desired pellet size for loading into the esterification reactor.

#### C. Catalyst Testing:

The reactor used was a three-zone Severn Sciences reactor constructed of Hastelloy C-276 capable of withstanding glacial acetic acid up to 300°C and 15000 Kpa (150 barg) pressure (length 650 mm, outer diameter 22 mm, internal diameter 16 mm). It had a thermowell running the entire reactor length (5 mm outer diameter) and 1.77 cm outer diameter Swagelock VCR joints at each end. Gas from cylinders of ethylene and nitrogen were taken off at 1000 Kpa (10 barg) and then compressed to 5000-12000 Kpa (50-120 barg), via Haskel boosters, before being regulated and fed to mass-flow controllers. The liquid feed systems had 2  $\text{dm}^3$  reservoirs maintained under a nitrogen blanket of 10 KPa-80 KPa (0.1-0.8 barg).

A cooling jacket was provided to condense products in the gas stream back to liquids prior to collection in a receiver. The majority of the liquid product was collected at room temperature.

A pre-heating zone was located upstream of the catalyst bed. The pre-heating zone was separated from the catalyst bed by a plug of glass wool. Another plug of gas wool was used downstream of the catalyst bed to reduce dead volume and help maintain the catalyst bed in the centre section of the reactor.

The reaction was started up by pressurising the reactor to 1000 KPa (10 barg) with nitrogen, establishing the desired flow rate (which is the same as that used later for the olefin feed) and then increasing the reactor temperature to the desired operating conditions (170°C or 180°C) over a one hour period. The liquid pump for the mixture of acetic acid/water mixture was switched on initially at the desired flow rate and the olefin admitted into the reactor on liquid breakthrough at the collection pots, usually after 2 to 3 hours. The flows were then adjusted to give the desired feed molar ratios and GHSVs. The reactor effluent was collected at regular intervals. Liquid product was drained off, weighed and then analysed by GC. The gas stream was sampled downstream of the liquid collection points and also analysed by GC. Total gas out during a test period was measured using a wet-gas meter.

The above process/catalysts were used to esterify ethylene with acetic acid. The relative amounts of each of these catalysts used, their bed size and bed length in performing the esterification reaction were as follows:

Parameter	Catalyst 1	Catalyst 2	Catalyst 3
Volume (cm <sup>3</sup> )	25	25	25
Weight (g)	11.3 (11.4*)	12	12
Pellet size (mm)	1-2 (0.5-1*)	0.5-1	0.5-1
Bed length	8.75 (14*)	14	14

\* Parameters of Catalyst 1 used for the Runs in Table 2

The reaction conditions used and the results achieved are tabulated below.

In these tables, the following abbreviations have been used:

HOS

Hours on stream

Bed (T/M/B)

Bed (top/middle/bottom)

HAC

Acetic Acid

	$C_2H_4$	Ethylene
	$H_2O$	Water
	EtAc	Ethyl acetate
	EtOH	Ethanol
5	DEE	Diethyl ether
	GHSV	Gas hourly space velocity
	g/Lcat/h	Gram per litre of catalyst per hour
	STP	Standard temperature & pressure
	STY	Space time yield

10

15

20

25

30

**TABLE 1****Run Conditions: (1 Mole % Water added to feed) using Catalyst 1:**

Parameters	Run No. 1	Run No. 2	Run No. 3*
HOS	17-20	42-45	70-73 (21-24)
Temperature (°C)			
Applied	170	170	170
Bed (T/M/B)	173/-/170	172.5/-/169.5	170/-/168
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	980	980	974. ----
C <sub>2</sub> H <sub>4</sub> GHSV/h	905	905	905
HAC GHSV/h	66	66	69
H <sub>2</sub> O GHSV/h	9	9	9
C <sub>2</sub> H <sub>4</sub> (g/Lcat/h)	1131	1131	1131
HAC (g/Lcat/h)	177	177	185
H <sub>2</sub> O (g/Lcat/h)	8	8	0
Feed contact time [1/GHSV](secs)	4	4	4
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O mole % ratio	92.3/6.7/1.0	92.3/6.7/1.0	92.9/7.2/0
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O wt % ratio	85.9/13.5/0.6	85.9/13.5/0.6	85.9/14.1/0
C <sub>2</sub> H <sub>4</sub> /HAC mole ratio	13.7	13.7	13.1

\* - No added water used in this comparative test (not according to the invention)

**Product Analysis (Table 1 continued):**

Products/Analysis	Run No. 1	Run No. 2	Run No. 3*
HAC Conversion	66	64	27
Product Selectivity (wt %)			
EtAc	97.3	97.8	91.6
EtOH	0.4	0.3	0.1
DEE	1.8	1.3	0.0
Acetaldehyde	0.0	0.0	0.0
Oligomers	0.3	0.6	1.4
Others	0.1	0.04	6.8
EtAc Yield	95	59	25
EtAc STY (g/Lcat/h)	180	160	44
Carbon Balance (mol %)	104	105	100
Oxygen Balance (mol %)	95	102	81
Mass Balance	103	105	99
Water recovered (%)	69	73	-

\* No water used and is hence a comparative test (not according to the invention)

**TABLE 2****Run Conditions: (1 Mole % Water added to feed) using Catalyst 1:**

Parameters	Run No. 4	Run No. 5	Run No. 6	Run No. 7
HOS	19-22	44-77	68.75-71.75	91-94
Temperature (°C) Applied Bed (T/M/B)	180 181.5/186/182. 5	180 181.5/185/183	180 181.3/184.5/181.2	180 181.4/184/181. 1
Pressure (Kpa)	1000	1000	1000	1000
Total feed GHSV/h (@ STP)	980	980	980	980
C <sub>2</sub> H <sub>4</sub> GHSV/h	905	905	905	905
HAC GHSV/h	66	66	66	66
H <sub>2</sub> O GHSV/h	9	9	9	9
C <sub>2</sub> H <sub>4</sub> (g/Lcat/h)	1131	1131	1131	1131
HAC (g/Lcat/h)	177	177	177	177
H <sub>2</sub> O (g/Lcat/h)	8	8	8	8
Feed contact time [1/GHSV](secs)	4	4	4	4
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O mole % ratio	92.3/6.7/1.0	92.3/6.7/1.0	92.3/6.7/1.0	92.3/6.7/1.0
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O wt % ratio	86/13.4/0.6	86/13.4/0.6	86/13.4/0.6	86/13.4/0.6
C <sub>2</sub> H <sub>4</sub> /HAC mole ratio	13.7	13.7	13.7	13.7

**Product Analysis (Table 2 continued):**

Products/Analysis	Run No. 4	Run No. 5	Run No. 6	Run No. 7
Ethylene conversion (%)	5.3	3.9	4.1	6.0
HAC Conversion	71	64	60	54
Product Selectivity (wt %)				
EtAc	95.9	97.2	97.8	98.1
EtOH	0.7	0.6	0.5	0.6
DEE	2.3	1.8	1.3	1.0
Acetaldehyde	0.0	0.0	0.0	0.0
Oligomers	0.8	0.3	0.3	0.2
Others	0.3	0.1	0.0	0.0
EtAc Yield	68	63	59	53
EtAc STY (g/Lcat/h)	194	183	164	148
Carbon Balance (mol %)	100	199	100	97
Oxygen Balance (mol %)	94	89	93	88
Mass Balance	100	99	99	96
Water recovered (%)	53	56	62	65

**TABLE 3**Run Conditions: (1 Mole % Water added to feed) using Catalyst 2:

Parameters	Run No. 8	Run No. 9	Run No. 10
HOS	14.75-17.5	38.5-41.5	62.5-65.5
Temperature (°C)	180	180	180
Applied Bed (T/M/B)	179.5/189/182.8	179.6/187.5/182.9	179.4/186.5/182.8
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	981	981	981
C <sub>2</sub> H <sub>4</sub> GHSV/h	905	905	905
HAC GHSV/h	66	66	66
H <sub>2</sub> O GHSV/h	10	10	10
C <sub>2</sub> H <sub>4</sub> (g/Lcat/h)	1131	1131	1131
HAC (g/Lcat/h)	177	177	177
H <sub>2</sub> O (g/Lcat/h)	8	8	8
Feed contact time [1/GHSV](secs)	4	4	4
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O mole % ratio	92.3/6.7/1.0	92.3/6.7/1.0	92.3/6.7/1.0
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O wt % ratio	85.9/13.5/0.6	85.9/13.5/0.6	85.9/13.5/0.6
C <sub>2</sub> H <sub>4</sub> /HAC mole ratio	13.7	13.7	13.7

Product Analysis (Table 3 continued):

Products/Analysis	Run No. 8	Run No. 9	Run No. 10
Ethylene Conversion	7.3	3.9	3.3
HAC Conversion	81	77	75
Product Selectivity (wt %)			
EtAc	92.7	95.2	96.0
EtOH	0.8	0.7	0.7
DEE	3.8	2.8	2.2
Acetaldehyde	0.0	0.0	0.0
Oligomers	1.6	0.9	0.8
Others	1.1	0.5	0.3
EtAc Yield	75	73	72
EtAc STY (g/Lcat/h)	213	211	201
Carbon Balance (mol %)	100	102	103
Oxygen Balance (mol %)	99	96	98
Mass Balance	100	102	103
Water recovered (%)	45	43	51

**TABLE 4**Run Conditions: (5 Mole % Water added to feed) using Catalyst 2:

Parameters	Run No. 11	Run No. 12	Run No. 13
HOS	90.5-95.5	134.5-137.5	158.5-161.5
Temperature (°C)	180	180	180
Applied Bed (T/M/B)	179.3/188.5/182.4	179.6/188.5/183.4	179.5/188.5/183.4
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	975	975	975
C <sub>2</sub> H <sub>4</sub> GHSV/h	866	866	866
HAC GHSV/h	61	61	61
H <sub>2</sub> O GHSV/h	48	48	48
C <sub>2</sub> H <sub>4</sub> (g/Lcat/h)	1083	1083	1083
HAC (g/Lcat/h)	164	164	164
H <sub>2</sub> O (g/Lcat/h)	38	38	38
Feed contact time [1/GHSV](secs)	4	4	4
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O mole % ratio	88.8/6.3/4.9	88.8/6.3/4.9	88.8/6.3/4.9
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O wt % ratio	84.2/12.8/3	84.2/12.8/3	84.2/12.8/3
C <sub>2</sub> H <sub>4</sub> /HAC mole ratio	14.2	14.2	14.2

Product Analysis (Table 4 continued):

Products/Analysis	Run No. 11	Run No. 12	Run No. 13
Ethylene Conversion	4.4	4.0	4.3
HAC Conversion	68	72	72
Product Selectivity (wt %)			
EtAc	85.2	82.9	82.0
EtOH	3.7	3.7	3.9
DEE	10.5	13.0	13.6
Acetaldehyde	0.0	0.0	0.0
Oligomers	0.6	0.4	0.5
Others	0.01	0.02	0.07
EtAc Yield	58	60	59
EtAc STY (g/Lcat/h)	203	215	210
Carbon Balance (mol %)	102	103	103
Oxygen Balance (mol %)	87	87	89
Mass Balance	101	102	102
Water recovered (%)	43	39	42

**TABLE 5**

Run Conditions: (5 Mole % Water added to feed) using Catalyst 3:

Parameters	Run No. 14	Run No. 15	Run No. 16
HOS	16-19	40-43	112.5-115.5
Temperature (°C) Applied Bed (T/M/B)	180 179.1/191/183.2	180 179.1/190.5/183.5	180 179.2/190/183.8
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	980	980	980
C <sub>2</sub> H <sub>4</sub> GHSV/h	866	866	866
HAC GHSV/h	64	64	64
H <sub>2</sub> O GHSV/h	50	50	50
C <sub>2</sub> H <sub>4</sub> (g/Lcat/h)	1083	1083	1083
HAC (g/Lcat/h)	170	170	170
H <sub>2</sub> O (g/Lcat/h)	40	40	40
Feed contact time [1/GHSV](secs)	4	4	4
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O mole % ratio	88.4/6.5/5.1	88.4/6.5/5.1	92.3/6.7/1.0
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O wt % ratio	83.7/13.2/3.1	83.7/13.2/3.1	86/13.4/0.6
C <sub>2</sub> H <sub>4</sub> /HAC mole ratio	13.6	13.6	13.6

Product Analysis (Table 5 continued):

Products/Analysis	Run No. 14	Run No. 15	Run No. 16
Ethylene Conversion	6.6	7.6	6.3
HAC Conversion	86	85	83
Product Selectivity (wt %)			
EtAc	73.4	74.0	73.2
EtOH	3.7	3.7	3.5
DEE	22.0	21.5	22.9
Acetaldehyde	0.0	0.0	0.0
Oligomers	0.6	0.7	0.5
Others	0.2	0.1	0.0
EtAc Yield	63	63	60
EtAc STY (g/Lcat/h)	219	221	224
Carbon Balance (mol %)	106	104	105
Oxygen Balance (mol %)	103	101	95
Mass Balance	105	104	104
Water recovered (%)	40	40	36



**TABLE 6**Run Conditions: (5 Mole % Water added to feed) using Catalyst 3:

Parameters	Run No. 17	Run No. 18	Run No. 19
HOS	160.5-163.5	208.5-211.5	285.5-288.5
Temperature (°C) Applied Bed (T/M/B)	180 179.2/190/184.1	180 179.3/190/184.3	180 179.3/190/184.2
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	980	980	980
C <sub>2</sub> H <sub>4</sub> GHSV/h	866	866	866
HAC GHSV/h	64	64	64
H <sub>2</sub> O GHSV/h	50	50	50
C <sub>2</sub> H <sub>4</sub> (g/Lcat/h)	1083	1083	1083
HAC (g/Lcat/h)	170	170	170
H <sub>2</sub> O (g/Lcat/h)	40	40	40
Feed contact time [1/GHSV](secs)	4	4	4
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O mole % ratio	88.4/6.5/5.1	88.4/6.5/5.1	88.4/6.5/5.1
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O wt % ratio	83.7/13.2/3.1	83.7/13.2/3.1	83.7/13.2/3.1
C <sub>2</sub> H <sub>4</sub> /HAC mole ratio	13.6	13.6	13.6

Product Analysis (Table 6 continued):

Products/Analysis	Run No. 17	Run No. 18	Run No. 19
Ethylene Conversion	8.8	8.7	8.4
HAC Conversion	85	86	88
Product Selectivity (wt %)			
EtAc	73.2	73.0	73.7
EtOH	3.6	3.9	3.7
DEE	22.6	22.6	22.1
Acetaldehyde	0.0	0.0	0.0
Oligomers	0.5	0.5	0.5
Others	0.1	0.1	0.1
EtAc Yield	62	63	65
EtAc STY (g/Lcat/h)	217	217	225
Carbon Balance (mol %)	104	104	104
Oxygen Balance (mol %)	103	103	103
Mass Balance	103	104	104
Water recovered (%)	40	41	38

**TABLE 7****Run Conditions: (5 Mole % Water added to feed) using Catalyst 3:**

Parameters	Run No. 20	Run No. 21*	Run No. 22*
HOS	375.5-378.5	448.5-451.5	472.5-475.5
Temperature (°C)			
Applied	180	180	180
Bed (T/M/B)	179.3/190/184.4	179.3/186.5/183.4	179.3/186.5/183.4
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	980	1001	1001
C <sub>2</sub> H <sub>4</sub> GHSV/h	866	866	866
HAC GHSV/h	64	64	64
H <sub>2</sub> O GHSV/h	50	50	50
DEE GHSV/h	0	21	21
C <sub>2</sub> H <sub>4</sub> (g/Lcat/h)	1083	1083	1083
HAC (g/Lcat/h)	170	170	170
H <sub>2</sub> O (g/Lcat/h)	40	40	40
DEE g/Lcat/h	0	71	71
Feed contact time [1/GHSV](secs)	3.7	3.6	3.6
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O/DEE mole % ratio	88.4/6.5/5.1§	86.5/6.4/5/2.1	86.5/6.4/5/2.1
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O/DEE wt % ratio	83.7/13.2/3.1§	79.4/12.5/2.9/5.2	79.4/12.5/2.9/5.2
C <sub>2</sub> H <sub>4</sub> /HAC mole ratio	13.6	13.6	13.6

\* co-fed additionally with 2 Mole % DEE.

§ - No diethyl ether used in this Run

**Product Analysis (Table 7 continued):**

Products/Analysis	Run No. 20	Run No. 21	Run No. 22
Ethylene Conversion	8.7	2.7	2.4
HAC Conversion	85	81	80
Product Selectivity (wt %)			
EtAc	74.1	71.9	70.8
EtOH	3.6	5.0	5.4
DEE	21.6	22.9	23.3
Acetaldehyde	0.0	0.0	0.0
Oligomers	0.5	0.2	0.5
Others	0.1	0.0	0.0
EtAc Yield	63	59	57
EtAc STY (g/Lcat/h)	226	226	222
Carbon Balance (mol %)	103	105	105
Oxygen Balance (mol %)	98	101	98
Mass Balance	102	105	104
Water recovered (%)	38	60	63

**TABLE 8**

Run Conditions: (5 Mole % Water + 2 Mole % DEE added to feed) using Catalyst 3:

Parameters	Run No. 23	Run No. 24
HOS	479.5-500.5	544.5-547.5
Temperature (°C)		
Applied	180	180
Bed (T/M/B)	179.3/186.5/183.4	179.4/187/183.4
Pressure (Kpa)	1000	1000
Total feed GHSV/h (@ STP)	1001	1001
C <sub>2</sub> H <sub>4</sub> GHSV/h	866	866
HAC GHSV/h	64	64
H <sub>2</sub> O GHSV/h	50	50
DEE GHSV/h	21	21
C <sub>2</sub> H <sub>4</sub> (g/Lcat/h)	1083	1083
HAC (g/Lcat/h)	170	170
H <sub>2</sub> O (g/Lcat/h)	40	40
DEE (g/Lcat/h)	71	71
Feed contact time [1/GHSV](secs)	3.6	3.6
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O/DEE mole % ratio	86.5/6.4/5/2.1	86.5/6.4/5/2.1
C <sub>2</sub> H <sub>4</sub> /HAC/ H <sub>2</sub> O/DEE wt % ratio	79.4/12.5/2.9/5.2	79.4/12.5/2.9/5.2
C <sub>2</sub> H <sub>4</sub> /HAC mole ratio	13.6	13.6

Product Analysis (Table 8 continued):

Products/Analysis	Run No. 23	Run No. 24
Ethylene Conversion	1.4	1.3
HAC Conversion	84	82
Product Selectivity (wt %)		
EtAc	70.6	71.1
EtOH	5.1	5.2
DEE	23.9	23.5
Acetaldehyde	0.0	0.0
Oligomers	0.3	0.3
Others	0.0	0.0
EtAc Yield	59	58
EtAc STY (g/Lcat/h)	226	224
Carbon Balance (mol %)	107	106
Oxygen Balance (mol %)	103	99
Mass Balance	106	105
Water recovered (%)	61	63

**TABLE 9**

LIQUID PRODUCT DATA			
GCMS			
180°C, 1000 Kpa (10 barg), ethylene/acetic acid = 14			
Organics (% by Wt)	Run No.		
	7	17	23
Water (mole% in feed)	1	5	5 (+ 2% DEE)
Acetic acid (unreacted feed)	52.3	21.2	16.3
Ethyl acetate	46.5	67.3	69
Diethylether	0.05	3	3.3
Ethanol	0.65	7.8	11
Acetaldehyde	0.002	0.04	0.009
C6 oligomers	0.0015	0	0
C8 oligomers	0.0055	0	0
Miscellaneous oxygenates	0.0065	0	0
Aromatic hydrocarbons	0.045	0	0
Unknowns	0.11	0.01	0
BALANCE :others (Hydrocarbons & oxy compounds)			